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Carboxymethyl starch cross-linked by electron beam radiation in presence of acrylic acid sensitizer

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Abstract Carboxymethyl starch (CMS) can be cross-linked by electron beam radiation to form a biocompatible and environment-friendly hydrogel at a high absorbed dose and a condensed CMS concentration. Acrylic acid (AAc) can be used as a sensitizer in order to reduce the absorbed doses to an acceptable certain level. At an absorbed dose of 3–4 kGy, the gel content of crosslinked CMS can be obtained about 50% with 5% (w/w) AAc concentration used. The compressive strength of CMS samples increased with increasing their cross-linked densities due to raising absorbed doses. The swelling ratio of cross-linked CMS was also attainable at a maximum of 50 times in the distilled water. The enzymatic degradation of cross-linked CMS was carried out in acetate buffer pH 4.6 with 0.1% α-amylase enzymatic solution incubated at 40ºC for 6 h. The crosslinked CMS samples were degraded slower than uncrosslinked CMS ones. The results indicated that the highly cross-linked CMS was almost fully degradable when the enzymatic hydrolysis was performed during 6 h. The FT IR spectra of cross-linked CMS in the presence of AAc were examined to observe the carboxyl group of AAc in the structure of cross-linked CMS. The hydrophilic of cross-linked CMS surface was determined by a contact-angle analysis.

Key words Sensitizer, Carboxymethyl starch, Crosslinking, Biodegradation, Electron beams, Radiation, hydrophilic.

1 Introduction

Crosslinked HEMA hydrogel investigated in 1960 with its hydrophilic character and biocompatible potential[1]. Later, hydrogels combined between natural and synthetic polymers have interested in the field such as controlled release drug, wound dressing, encapsulation of cells, tissue engineering, matrices for repairing and regenerating a wide variety of tissue and organs[2,3]. Hydrogels are called chemical gels when they are covalently crosslinked networks. Hydrogel can absorb from dozens of times up to thousands of times its dry weight in water[4]. Polysaccharide derivative hydrogels may be crosslinked by irradiation at paste-like conditions. Hydrogels can form from radiation crosslinking of carboxymethyl cellulose (CMC), carboxymethyl starch, carboxymethyl chitin and carboxymethyl chitisan at condensed concentrations (higher than 10%). These hydrogels swelled well in water and were biodegradable[5]. Radiation crosslinking of carboxymethyl starch (CMS) was carried out at paste-like concentration (20–50%). It was proved that the amylopectin region in CMS was predominantly responsible for crosslinking of CMS[6]. The gel strength of CMC treated in irradiation combination (5–10 kGy) with acid immerse was 100 times higher than that of CMC untreated with acid[7]. Relationship between structure and drug release of CMS has mutual influence of drying procedures and of its degree of substitution[8]. Biodegradability of blend hydrogels based on CMC and CMS was evaluated. The ratio of CMC part to CMS one in the blend was influenced on radiation crosslinking characterizations such as gel fraction, swelling degree, gel strength and biodegradability[9]. Electron beam crosslinking of CMS at high absorbed dose of 50 kGy, at 50% (v/v) concentration has been investigated with gel content

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obtained max. 87.1%. Radiation crosslinked CMS was used to remove iron in aqueous solution[10].

2 Eperimental

2.1 Materials

Sodium carboxymethyl starch EMSIZE CMS-150 (M_w=600 kDa, *DS*=0, 85, Emsland Stärke, Germany); α-amylasa enzyme (Himedia, India); acrylic acid (BASF, Germany); acetic acid, sodium acetate, calcium chloride ($CaCl_2$) (China); distilled water were used during the experiment.

2.2 Preparation of CMS hydrogel

The formulation of 35% CMS and 1% AAc was prepared as follows: weighing 350 g of CMS powder put into a 2 L beaker with 650 mL of distilled water available. The mixture was stirred at room temperature for 2 h to get a homogeneous state, and then 9.5 mL of AAc was added while the system was going on stirring further for 1 h. The paste-like CMS mixture was packed in polyethylene bags and stood for overnight before irradiated on electron beam accelerator with 10 MeV and 15 kW power (UERL-10-15S2, Russia) at absorbed doses of 3.5, 7.0, 10.5 and 14 kGy. Drying the sample was performed at 70ºC for 15 h. Hence the dried CMS was ground into 300 mesh particles. Similarly, samples of 35% CMS with an addition of 3% and 5% AAc were also formulated. Blank sample of 35% CMS without AAc was prepared following the above mentioned steps.

2.3 Determination of characteristic properties of crosslinked CMS

2.3.1 Gel content

0.15 g of sample covered by stainless steel net was extracted in a Soxhlet instrument with distilled water as solvent for 24 h. The sample was dried in an oven at 70ºC for overnight, kept in desiccators in 4 h before weighing. The gel content was impressed as follows.

$$\textit{Gel content}\ (\%) = (W_g/W_i)\times 100$$

where W_i and W_g are the weights of initial dry CMS and of extracted dry CMS with hot water, respectively.

2.3.2 Swelling ratio

0.5 g of sample was weighed and immersed in 100 mL of distilled water for 48 h. The swollen CMS gel was taken out, excessive water on surface of the sample absorbed with tissue paper and then weighed. The swelling ratio (the amount of water absorbed by the CMS gel) was defined as follows:

$$\textit{Swelling ratio}\ (\text{g/g}) = (W_s - W_g)/W_g$$

where, W_s is the weight of the swollen CMS gel.

2.3.3 Compressive strength

The strength of the gel immersed in water was tested on a Strograph V 10-C tester (Toyoseiki, Japan). Maximum stresses at 50% compression were measured for cylindrical formed gel.

2.3.4 Enzymatic degradation

25 mg of sample was weighed and put in tubes with screwed caps containing 4 mL of acetate buffer solution at pH 4.6, 1 mL of 0.1% $CaCl_2$ solution and 1mL of 0.1% α-amylase enzymatic solution (10^6cfu/mL). The tubes were incubated at 40ºC in thermostat bath. The experimental cycle was carried out for 6 h, every one hour; one sample was taken out, filtered by filter paper, washed by distilled water for some times, dried at 70ºC for overnight, stored in desiccators in 4 h and then weighed whenever its weight was constant. Loss of CMS gel weight was determined as follows:

$$M\ /\ \% = [(m_0 - m_1)/m_0]\times 100$$

where, M, m_0 and m_1 are the weight percentage of lost dry CMS gel, weight of initial dry CMS gel and of residual dry CMS gel, respectively.

2.3.5 FT IR spectra

FT IR spectra of the gel with 3% AAc and without AAc that were irradiated at 10.5 kGy were measured by FT IR 8400S spectrophotometer (Shimadzu, Japan).

2.3.6 Hydrophilic (wetting property) analysis

Contact angle measurement of swollen CMS gel membranes with AAc at various concentrations and without AAc was performed on the Contact Angle System OCA (Dataphysics Instruments, GmbH, Germany) at 25ºC.

3 Results and discussion

3.1 Gel content

Figure 1 shows the change of EB absorbed doses in gel content of CMS in the presence of acrylic acid sensitizer at concentrations of 0, 1, 3, 5% (w/w). Gel

content of CMS increases with increasing absorbed doses and AAc concentration. At the optimal dose of around 3–4 kGy, a gel content can be obtained 60%; except 5% lower AAc concentrations, gel contents are attainable at a low value of 20%–30% at 7 kGy. Without AAc used, the gel content in crosslinked CMS is the lowest.

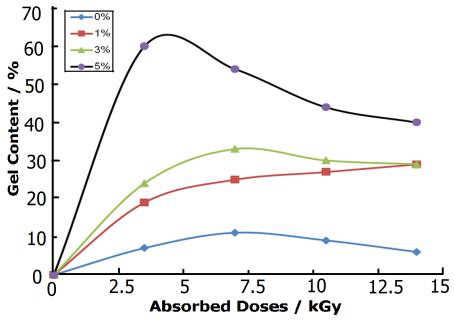

Fig.1 Change of absorbed doses in gel content of CMS in the presence of acrylic acid sensitizer at various concentrations.

3.2 Swelling ratio

Figure 2 shows the effect of absorbed doses on swelling ratio of CMS in the presence of acrylic acid sensitizer at concentrations of 0%, 1%, 3%, 5%. When the water absorbed reduces with increase of absorbed doses and of AAc concentration. It is true to crosslinking theory of a predominant crosslinked polymer. The swelling ratio of CMS gel decreases to a minimum at 3–4 kGy. At doses higher 5 kGy the water absorbed in CMS gel almost unchanges. It can be explained that crosslinked CMS gel makes network space in network structure in the gel smaller. When the doses increase higher 10 kGy with increase of water uptake of CMS without AAc due to a partly degradation of CMS gel.

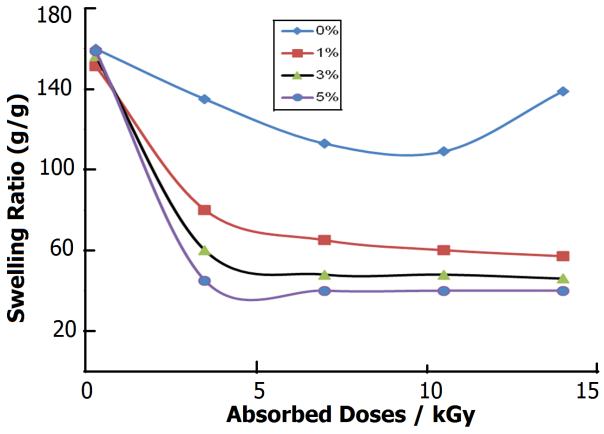

Fig.2 Effect of absorbed doses on swelling ratio of CMS in the presence of acrylic acid sensitizer.

3.3 Compressive strength at 50% compression

Figure 3 shows relationship between EB absorbed doses and maximum stress at 50% compression of CMS gel (sometimes so-called gel strength) with different AAc oncentrations. The gel strength of CMS gel increases with increasing the doses. The increase of AAc concentration also leads to go up the strength. It means that the gel strength increases with a higher durability of the gel due to increased crosslinking as seen in Fig.3.

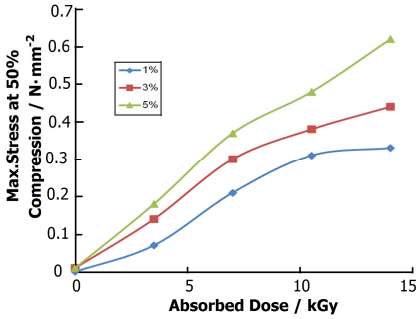

Fig.3 Relationship between EB absorbed doses and maximum stress at 50% compression of CMS gel with different AAc concentrations.

3.4 Enzymatic degradation of CMS gel

Figure 4 shows hydrolysed time of CMS gel at various EB absorbed doses versus weight loss of CMS gel. The slow hydrolyzation of CMS gel with α-amylasa enzyme at 3.5 kGy absorbed dose and 5% AAc concentration reveals that the crosslinking of CMS gel was optimal if compared to other CMS gels at higher absorbed doses (7, 10.5, 14 kGy) and lower AAc concentrations (1 and 3%), which were anticipated to be a certain region of CMS gel radiation -degraded at high doses. It is presented that crosslinked CMS gels added AAc sensitizer probably degraded in enzymatic media at a significant level.

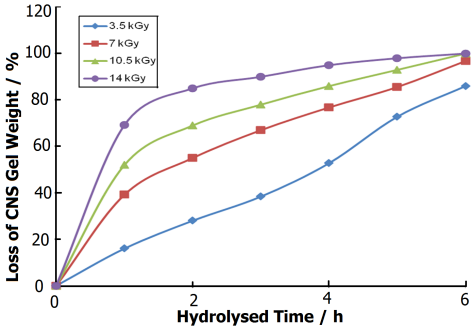

Fig.4 Hydrolysed time of CMS gel at various EB absorbed

doses vs. weight loss of CMS gel at 5% AAc concentration.

3.5 FT IR spectra

Figure 5 shows the FTIR spectra of CMS with or without AAc sensitizer. A peak at 1728 cm^{-1} is assigned to carboxyl group (-COOH) of acrylic acid in CMS chain. Other peak appearred at 1161 cm^{-1} is referred as -C-O group in CMS.

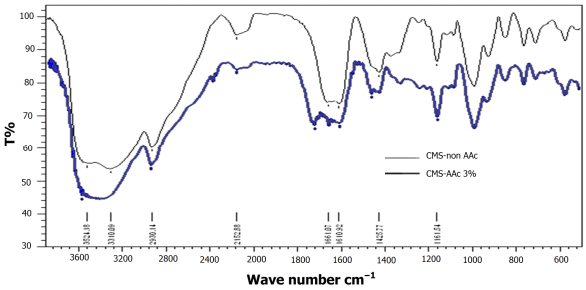

Fig.5 FT IR spectra of CMS without AAc and with 3% AAc.

3.6 Wetting property of CMS gel membrane

Figure 6 shows the effect of absorbed doses on wettability of CMS gel membrane at 5% AAc concentration measured indirectly by contact angle technique. Contact angle measured for CMS gel increase with increasing the absorbed doses. It means that hydrophibility of CMS gel membrane reduces with increased its crosslinking ability at 5% AAc concentration. It suggests that the selection of a suitable EB absorbed dose for a practical application of CMS gel such as cosmetics and personal care (face mask) should have a highly relative wettability.

4 Conclusion

AAc plays a essential role of a sensitizer for reduction of absorbed doses in EB radiation crosslinking of CMS. The studying results indicated that AAc accelerates CMS crosslinking through making an increase of gel content and gel strength of CMS gel but an decrease of swelling ratio, enzymatic degradability and wettability of CMS gel. The CMS gel with physical characters comprising 60%–70% gel content and 70–80 (g/g) swelling ratio can be formed by EB radiation crosslinking at 35 % CMS, 3%–5% AAc concentration at 3–4 kGy absorbed dose.

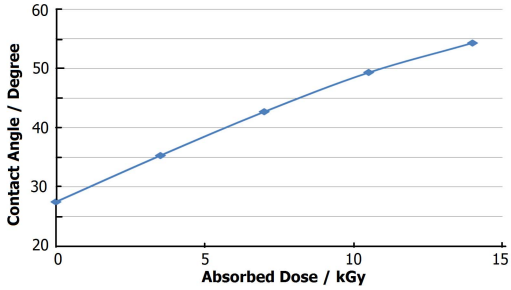

Fig.6 Effect of absorbed doses on wettability of CMS-AAc 5% gel membrane measured indirectly by contact angle technique at 25°C

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